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Study on the Inclusion Compounds of Eugenol with α-, β-, γ- and Heptakis (2,6-di-*O*-methyl)-β-cyclodextrins

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Abstract

Several host–guest inclusion compounds of eugenol as a guest molecule and cyclodextrins (α-,β-,γ-CD) and heptakis (2,6-di-*O*-methyl)- β-cyclodextrin (DMβ-CD) as hosts were investigated in the solid state and in aqueous solution. The one-to-one solid inclusion compounds of eugenol and β-CD or γ-CD were prepared, but those of eugenol with α- or DMβ-CD were not obtained under the same condition. However, the UV-visible absorption spectroscopy data indicated that the liquid guest could form a 1:1 inclusion compound with all four hosts respectively in aqueous solution. The two solid inclusion compounds were characterized by powder X-ray diffraction (XRD), infrared spectroscopy (IR), thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR). The association constants (*K*), calculated from the modified Benesi–Hidebrand equation, of eugenol with α-, β-, γ- and DMβ-CD is 4.95×10^4, 3.96×10^5, 1.47×10^5 and 9.33×10^4 mol^{-1} dm^3, respectively.

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six or more glucose units connected by α-1,4 linkages [1]. They have a hollow truncated shape. The three common CDs are α-, β- and γ-Cyclodextrins which are composed of 6, 7 and 8 glucose units respectively. The structure of the CDs is shown in Figure 1. As consequence of these structural features, CDs are capable of forming inclusion compounds with a variety of guests with low molecular weights [2–6]. The complexation of guest with cyclodextrins has been widely used to improve both the dissolution rate and absorption of poorly soluble materials [7]. CDs also have some advantages in other areas, such as the food, cosmetic industries and agrochemistry, especially owing to their capacity to protect the guest molecules against oxidation, light-induced reaction and loss by evaporation [8, 9].

Many papers have been published for the inclusion compounds of CDs till now. Although a lot of the selected guest molecules usually exist in solid state [10–11], many inclusion complexes of cyclodextrins with liquid guests, such as aliphatic alcohols and phenols, have also been reported [12]. Several crystal structures of the α- and β-cyclodextrin inclusion compounds with substituted phenols have been determined. Divakar and Maheswaran [13] reported an important structural studies on the inclusion compounds of β-cyclodextrin with some substituted phenols such as guaiacol, catechol and eugenol, suggesting that the guest molecules exhibit identical orientations – with the phenyl ring within the cavity and the hydroxyl and methoxyl groups projecting outside.

Clove oil and eugenol are known fish anesthetics and are also effective snake repellents. Eugenol (Figure 2), a colorless to pale yellow liquid with strong aromatic odor of clove having very poor solubility in water, was selected as a guest molecule in this study in order to further realize the inclusion phenomena of a slightly water-soluble oil organic molecule with several CDs possessing different cavity diameter in solid state and in aqueous solution.

The eugenol was mixed with α-, β-, γ- and DMβ-CD respectively in water, stirred 24 h at 293 K, and then separated and dried *in vacuo*. It is very interesting that the solid inclusion compound of eugenol with β- and γ-CD have been prepared whereas the solid complexation of eugeonl with α- and DMβ-CD were not obtained under the same experimental condition.

A lot of experimental techniques have been employed in determination of the binding affinity between cyclodextrin and guest molecules such as NMR [14, 15], UV-visible spectroscopy [16, 17] and etc. In this paper the solid inclusion compounds were investigated by using XRD, IR, TG, DSC and NMR spectroscopy. To further realize the relation between binding ability of host-guest and diameter of the host cavity, the complexation behavior of the eugenol with α-, β-, γ- and DMβ-CD was examined by UV-visible in aqueous solution. The obvious absorption changes of eugenol have been observed with or without CDs including α- and

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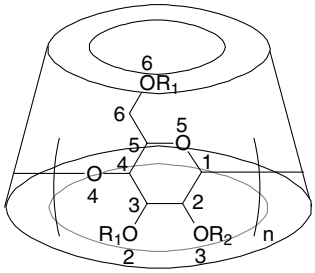

$n = 6$; $R_1 = R_2 = OH$, α-CD
$n = 7$; $R_1 = R_2 = OH$, β-CD
$n = 7$; $R_1 = OCH_3$, $R_2 = OH$, DMβ-C-CD
$n = 8$; $R_1 = R_2 = OH$, γ-CD

Figure 1. Schematic drawings of α-, β- and γ-CD.

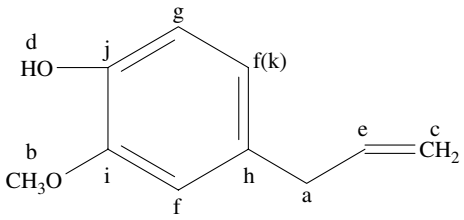

Figure 2. Molecular structure of the eugenol.

DMβ-CD although we cannot get solid inclusion compounds of them. By this token eugenol can form supermolecule with α- or DMβ-CD in aqueous solution. The *K* values of the association constant of eugenol with four host molecules, which is 4.95×10^4, 3.96×10^5, 1.47×10^5 and 9.33×10^4 mol^{-1} dm^3 respectively to α-, β-, γ- and DMβ-CD, are not significantly different, but they are much higher than those of phenol or some single substituted phenols such as *o-, m-* and *p*-nitrophenol with parent CDs [12]. The association constant of eugenol with β-CD or γ-CD is slightly bigger than that of eugenol with α-CD or DMβ-CD. The magnitude of *K* values may suggest that the matching between cyclodextrin cavity volume and guest dimension has a great influence on the formation and stability of inclusion compound of a substituted phenol.

Experimental

Materials

All chemicals were of general-purpose reagent grade unless otherwise stated. β-CD was purchased from Shanghai Chemical Reagent Company and recrystallized twice from water. α-CD was purchased from Nihon Toshin Chemical Company. γ- and DMβ-CD were kindly donated by Harata. Eugenol was purchased from Shanghai Feixiang Chemical Company and used without further purification.

Preparation of the solid inclusion compounds

The inclusion compounds were prepared by mixing eugenol with α-, β-, γ- or DMβ CD respectively in distilled water, and stirring 48 h at 293 K. The original molar ratio of eugenol and CDs was 10:1. The separated solid inclusion compounds were washed by using water and alcohol (95%) three times respectively and dried over 24 h at 383 K *in vacuo*. The solid inclusion compound of eugenol with α- or DMβ-CD cannot be found after stirring 48 h at 293 K. It is possible that since DMβ-CD is highly soluble in water, its inclusion compound of eugenol may also dissolve easily in aqueous solution. The stoichiometry of the solid complexes of β- and γ-cyclodextrin was determined to be 1:1 based on elemental analyses of the two samples (β-CD-eugenol complex, Anal. Calcd. for $C_{52}H_{82}O_{37}{\cdot}5H_2O$: C, 44.96; H, 6.63. Found: C, 45.36; H, 7.10. γ-CD-eugenol complex, Anal. Calcd. for $C_{58}H_{92}O_{42}{\cdot}6H_2O$: C, 44.39; H, 6.64. Found: C, 44.52; H, 6.74).

Characterization of the solid inclusion compounds

X-Ray powder diffraction (XRD) of the samples was reached on a Philips ŔPert Pro X-ray diffractometer. The samples were irradiated with monochromatized CuK_α and analyzed with $5° \le 2\theta \le 40°$. The voltage and current are 40 kV and 40 mA respectively.

Infrared (IR) spectra were recorded on Bruker EQUINOX55 spectrometer and obtained from KBr pellets in the 4000–400 cm^{-1} regions.

Thermogravimetric (TG) curves were recorded on Shimadzu TGA-50 thermogravimetric analyzer with heat rate of 10.00 K/min under a nitrogen atmosphere. Differential-scanning calorimetry curves (DSC) were measured on a Shimadzu DSC-50. The sample mass in an aluminum pan with lid use a heating rate of 10 K/min under nitrogen atmosphere in the temperature range of 0–500 K.

Elemental analyses were made using a Elementar Vario EL- elemental analyzer.

Nuclear magnetic resonance (^1H NMR and ^{13}C NMR) spectra were obtained on Bruker NMR spectrometer at 300 MHz at 293 K, using DMSO-d_6 as solvent and TMS as internal reference.

UV-visible absorption spectra of eugenol with and without α-, β-, γ-, DMβ-CD were recorded with Shimadzu UV 2401-(PC) UV/VIS spectrophotometer.

Results and discussion

X-Ray analysis

The diffraction patterns of eugenol, β-CD, γ-CD and their inclusion compounds are shown in Figure 3. Because eugenol is an oil liquid, there was no X-ray powder diffraction data available.

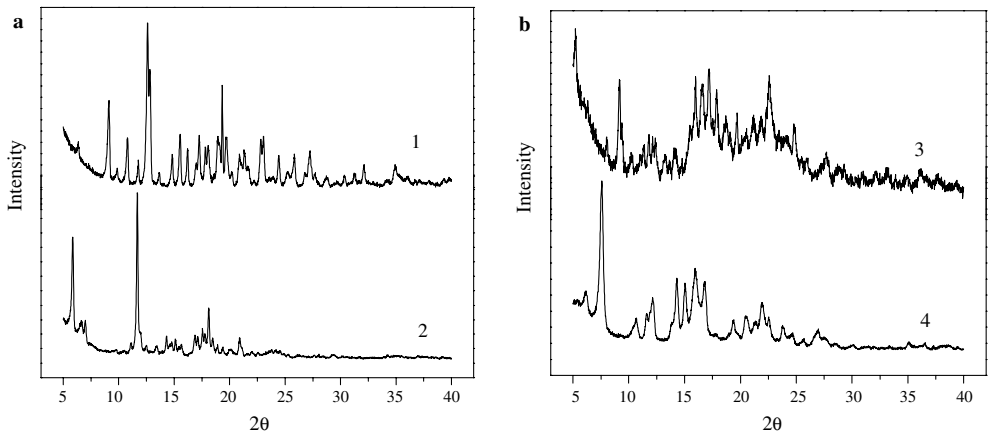

Figure 3. XRD spectra: (a) β-CD-eugenol system: 1. β-CD; 2. β-CD compound (b) γ-CD-eugenol system: 3. γ-CD; 4. γ-CD compound.

In Figure 3(a) the XRD diffraction spectrum of eugenol-β-CD inclusion compound shows considerable diversity when comparing with XRD diffraction of pure β-CD. The intensity of the top three peaks is 9.2, 12.7, 19.3 respectively in β-CD and they become 5.9, 11.7, 18.0 in eugenol-β-CD inclusion compound. Moreover the three top peaks of eugenol-β-CD inclusion compound shifted to lower 2θ angle range comparing with pure β-CD. And the intensity and location of the second and third XRD diffraction peaks between eugenol-β-CD inclusion complex and β-CD are prominently different. These results may suggest the formation of the solid β-CD inclusion compound. The crystalline patterns of the β-CD may change when a guest molecule has been in the cavity of the host molecule. In Figure 3(b), there are also some differences in the XRD diffraction of γ-CD and eugenol-γ-CD inclusion compound. The peaks are separate and there are no obvious top peaks. But the several relatively strong peaks of the eugenol-γ-CD inclusion compound also shift to lower 2θ angle range.

Cortes and his co-workers [17] investigated β-CD-chlorhexidine inclusion system and reported that the inclusion compound XRD shows a more amorphous when compared to the XRD of the free components and physical mixture. They deduced a disorder phenomenon upon inclusion. But it does not seem to support the conclusion from Figure 3 especially situated in lower 2θ angle range.

IR spectra analysis

The IR spectra of β-CD, γ-CD, eugenol and their inclusion compounds are shown in Figure 4. In Figure 4(a), pure β-CD shows prominent peaks at 3417.57 cm^{-1} and 1027.97 cm^{-1} due to υOH and υC—O of β-CD. And there are a series of peaks in 720-1250 cm^{-1} which is the fingerprint region of νC=C. In the IR spectrum of eugenol, it gives sharp peaks at 1638.09, 1612.23 and 1514.07 cm^{-1} that can contribute to the υC=C stretching of the aromatic moiety of eugenol.

In Figure 4 as for the eugenol-β-CD inclusion complex there have two peaks at 1638.09 and 1515.89 cm^{-1} that is the υ(C=C) of aromatic moiety, which also exists in the IR spectrum of free eugenol. The peaks of C=C stretching of the aromatic only give a

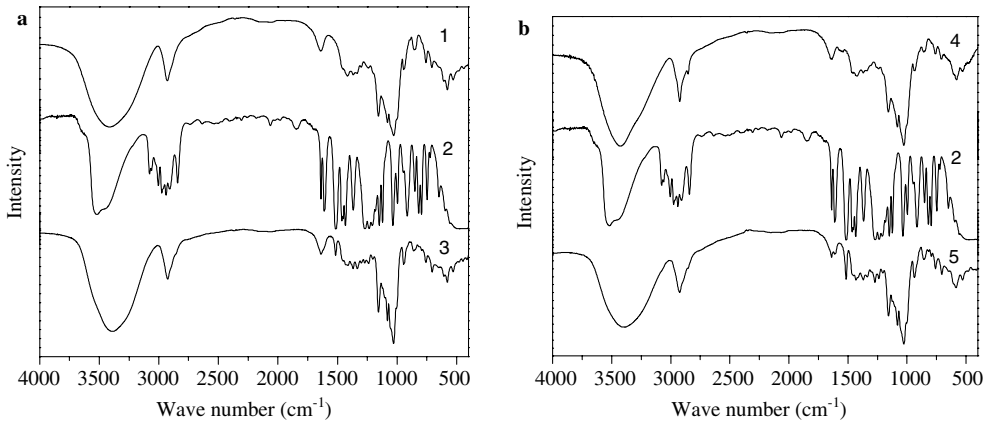

Figure 4. FT-IR spectra of (a) β-CD-eugenol system: 1. β-CD; 2. eugenol; 3. eugenol-β-CD inclusion compound; (b) γ-CD-eugenol system: 4. β-CD; 2. eugenol; 5. eugenol-γ-CD inclusion compound.

very low strength in Figure 4 because the quantities of eugenol are no more than 15% (w/w) in its inclusion compound, which was easily cover up by the peaks of β-CD. The υ (C=C) of aromatic moiety occurs at 1637.99 and 1515.20 cm^{-1} in eugenol-γ-CD inclusion compound. The C=C vibration stretching of the inclusion complex also gives a weak absorption. These results indicated that the eugenol might be included into the hydrophobic cavity of CDs.

Thermogravimetric (TG) analysis

TG curves of β-CD and its eugenol inclusion compound are shown in Figure 5. Because eugenol is an oil liquid, there is no TG curve for eugenol. The TG curves of β-CD and the inclusion compound of β-CD were very similar. In Figure 5(a) the first weight loss of β-CD and eugenol-β-CD inclusion compound is around 373 K, which can be explained as the release of water from the β-CD cavity, and the second weight loss around 573 K due to the decomposition of the β-CD. But there are some slight differences between them: the weight loss of eugenol-β-CD inclusion complex is more than that of β-CD under some certain temperature range. It may indicate the gradual release of the oil guest from the β-CD cavity at higher temperature. In the meanwhile a chemical reaction of eugenol, such as oxidation, might occur at high temperature during TG and DSC measurement. But in respect that the relative quantities of eugenol are so small in the solid inclusion compounds that the curves of the inclusion compounds are similar to those of the CDs.

Though the quantities of eugenol are very small relative to host in the inclusion compound, the results from XRD and IR have confirmed the existence of eugenol in the complexation. Therefore, it is reasonable that there is no obviously change of TG curves between eugenol-β-CD inclusion compound and β−CD. By the way the TG curves of γ-CD and eugenol system were the same as those of β-CD and its eugenol inclusion compounds.

DSC curves of β-CD and its eugenol inclusion compound are shown in Figure 6. The endothermic peak of β-CD was at 588.61 K. The endothermic peak appeared at 582.34 K for the eugenol-β-CD inclusion compound.

The eugenol was mixed with α-, β-, γ- and DMβ-CD respectively in water, stirred 24 h at 293 K, and then separated and dried *in vacuo*. It is very interesting that the solid inclusion compound of eugenol with β- and γ-CD have been prepared whereas the solid complexation of eugeonl with α- and DMβ-CD cannot be found under same experimental condition. However, the formation of the four inclusion compounds of eugenol with α-, β-, γ- and DMβ-CD have been confirmed based on the UV-visible investigations in aqueous solution. The cavity volume and solubility in water at room temperature of α-, β- and γ-CD is 174, 262, 427 Å and 14.5, 1.85, 23.2 g·100 ml^{-1} respectively. These results indicated the cavity size of β- and γ-CD are large enough that they can form the inclusion complex with eugenol while the cavity of α-CD is so small that it is difficult for eugenol to enter into the cavity. Furthermore, the solubility of host in water may not play an important role in forming a complexation between oil guest and the parent CDs. As for DMβ-CD, since it is highly soluble in water, it is possible that its inclusion compound of eugenol is also highly soluble in aqueous solution. Moreover, seven-OCH_3 with larger size around both end side of DMβ-CD cavity may to the extent retard the formation of the solid inclusion complex.

The results of ^{1}H NMR and ^{13}C NMR of β-CD, γ-CD, eugenol and their inclusion compounds are shown in Tables 1 and 2 respectively. ^{1}H NMR is an important

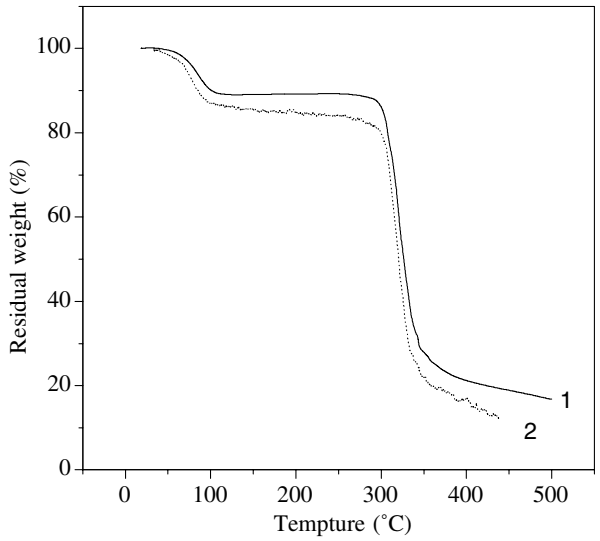

Figure 5. TG curves of β-CD-eugenol system:1. β-CD; 2. eugenol-β-CD inclusion compound.

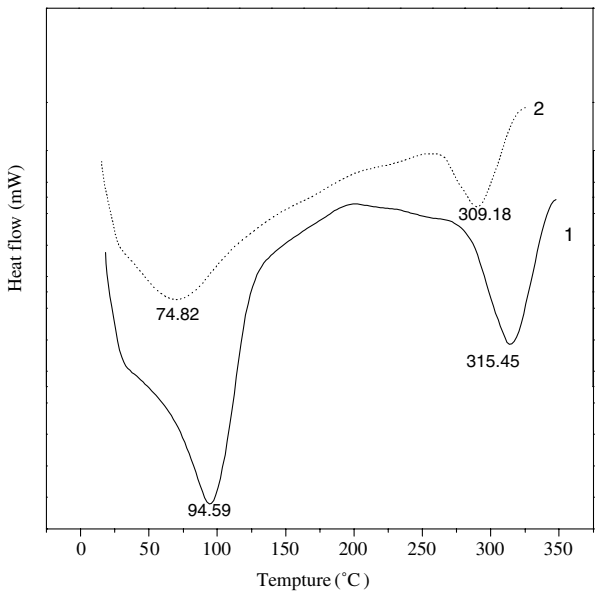

Figure 6. DSC curves of β-CD-eugenol system: 1. β-CD; 2. eugenol-β-CD inclusion compound.

technique in studying CDs inclusion compounds because the chemical shift (δ) of the cyclodextrin and guest protons related to the strength of cyclodextrins-guest interaction [6]. The ^{1}H NMR data clearly show the chemical shift change ($\Delta\delta$) of β-CD, γ-CD and euegnol spectra with and without inclusion action (Table 1).

^{13}C NMR chemical shifts extend over a much larger scale than proton shifts and particularly suited to identify the formation of CDs. In Table 2, the chemical shift changes $\Delta\delta$ from -0.333 to -0.226 ppm were observed for the shielding phenomena to all β-CD carbons from the phenyl of eugenol. The results listed in Tables 1 and 2 for γ-CD-eugenol system are similar to those listed in Table 1 and Table 2 for β-CD-eugenol system.

The chemical shifts (δ) of both the interior protons of CD (H-3 and H-5) and the guest protons can be analyzed to provide information about the inclusion mode and binding affinity between CD and guest. It was found that the change of chemical shift (δ) of H-3 located in large end side of cavity is bigger than that of H-5 located in small end side of cavity from the data listed in Table 1 and Table 3, suggesting that the phenyl ring of the guest molecule within the cavity may lay aboard large end side of cavity to the extent, the allyl group of the guest project outside from one end side of cavity and hydroxyl and methoxyl groups outside from the other end side of cavity. In view of the situation, polarization and size between hydroxyl or methoxyl groups and allyl it may be reasonable that the allyl group of the guest project outside from small end side of the cavity of CD.

NMR spectra were all measured in DMSO-d_6, DMSO-d_6 was selected as solvent in order to dissolve β-CD, γ-CD, eugenol (poorly soluble in water) and their solid inclusion compounds respectively. Although the solid inclusion compounds that we used in ^{1}H NMR and ^{13}C NMR experiments were previously prepared in aqueous solution, it is noteworthy that the complexation ability of cyclodextrins and their derivatives may be lower in DMSO than in D_2O and the geometry of inclusion may also change.

UV-visible spectroscopy

To further investigate the relation between binding affinity of host-guest and diameter of the host cavity, the complexation behavior of the eugenol with α-, β-, γ- and DMβ-CD was examined by UV-visible spectroscopy. The absorption spectra of eugenol in the absence and the presence of different concentrations of CDs are shown in Figure 7. In this experiments the concentration of the eugenol was 1×10^{-5} M and the concentration of CDs varied from 1×10^{-5} to 1×10^{-4} M. The obvious absorption changes of eugenol have been observed with or without CDs including α- and DMβ-CD although we cannot get the solid inclusion compounds of them. By this token eugenol can form supermolecule with α- or DMβ-CD in aqueous solution.

The absorption of eugenol gradually decreased in intensity upon addition of varying amounts of CDs. The associate constant (K) of eugenol with α-, β-, γ- and DMβ-CD can be calculated by applying the modified

Table 1. ^{1}H NMR chemical shifts, δ (ppm), of the C—H protons in β–CD, γ-CD, eugenol and the chemical shift changes ($\Delta\delta$) of β-CD, γ-CD and euegnol spectra with and without inclusion in DMSO-d_6

Position	β-CD		γ-CD			Eugenol		
	Free	$\Delta\delta$	Free	$\Delta\delta$	Position	Free	$\Delta\delta$	$\Delta\delta$
H-1	4.81	0.014	4.859	0.027	H-a	3.258	0.016	0.002
H-2	3.322	−0.002	3.306	0.005	H-b	3.733	−0.002	0.002
H-3	3.657	0.014	3.755	−0.12	H-c	5.02	−0.002	−0.003
H-4	3.294	−0.004	3.327	0.006	H-d	5.4	0	0
H-5	3.598	−0.048	3.567	−0.041	H-e	5.91	0.01	0.015
H-6	3.631	0.003	3.627	0.008	H-f	6.572	−0.004	−0.004
					H-g	6.721	−0.004	0.038

Table 2. ^{13}C NMR chemical shifts,δ(ppm), of β-CD, γ-CD, eugenol and the chemical shift changes ($\Delta\delta$) of β-CD, γ-CD and euegnol spectra with and without inclusion in DMSO-d_6

Position	β-CD		γ-CD		Position	Eugenol		
	Free	$\Delta\delta$	Free	$\Delta\delta$		Free	$\Delta\delta$	$\Delta\delta$
C-1	102.302	−0.247	102.22	−0.2	C-a	39.523	0.004	0.02
C-2	72.411	−0.27	73.01	−0.1	C-b	55.767	−0.147	0.11
C-3	73.47	−0.333	73.43	−0.21	C-c	115.742	0.002	−0.05
C-4	81.902	−0.24	81.41	−0.16	C-e	138.354	−0.091	0.12
C-5	72.73	−0.226	72.68	−0.22	C-f	120.906	−0.248	−0.03
C-6	60.319	−0.302	60.54	−0.24	C-g	112.848	−0.157	0.01
					C-h	130.844	−0.3	0.08

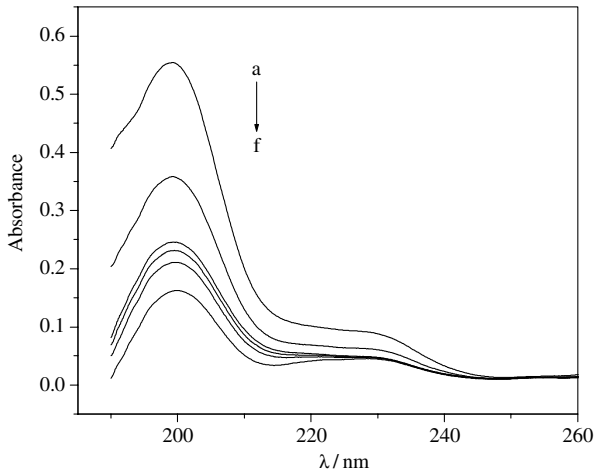

Figure 7. UV/vis absorption spectra of eugenol (1×10^{-5} M) in the absence and presence of β-CD. The concentration of β-CD (from a to f) is 0, 1, 2, 3, 4 and 5×10^{-5} M respectively.

Benesi–Hidebrand treatments to the UV-visible absorption [18].

For the calculation of association constants (K) base on the absorption spectra the Benesi–Hidebrand equation in the following form was used [16]:

$$\frac{[G] \cdot [\mathrm{CD}]}{\triangle A} = \frac{1}{Ks \cdot \triangle \varepsilon} + \frac{1}{\triangle \varepsilon}([G] + [\mathrm{CD}]) \qquad (1)$$

where [G] is the concentration of guest molecule, eugenol. [CD] is the concentration of α-, β-, γ-, and DMβ-CD respectively, $\triangle\varepsilon$ is the difference between the extinction coefficients of solution of associated and non associated eugenol, $\triangle$A is the difference between the absorbance of solutions of associated and non associated eugenol and K is the association constant of the complexation between eugenol and CDs.

The experimental data from Figure 7, i.e. β-CD-eugenol system were by and large fitted to the Benesi–Hidebrand equation by using the linearing repression method. In all other systems the dependencies were also linear, which indicated that 1:1 complexes are mainly formed in the systems studied. The K of eugenol with α-, β-, γ- and DMβ-CD is 4.95×10^4, 3.96×10^5, 1.47×10^5 and 9.33×10^4 mol^{-1} dm^3 respectively.

The K of eugenol with β-CD is bigger than that of eugenol with the other parent CDs or the β-CD derivative. It suggests that the cavity size of β-CD is fit enough for molecular volume of the eugenol that it can form the more steady inclusion compound with eugenol while the cavity of α-CD is so small that it is difficult for eugenol to enter into the cavity. Since the cavity of γ-CD is too large that it is not easy for eugenol to keep in the cavity. These demonstrate that the cyclodextrin cavity size has a great influence on the formation of inclusion compound. As for DMβ-CD, structurally it is obvious that seven -OCH_3 group around both end side of the cavity retarded to a certain extent the formation of the inclusion compound. The magnitude of the K values of eugenol with α-, β-CD is much higher than that of phenol with α-CD ($<10^2$ mol^{-1} dm^3) [12, 19, 20] or β-CD ($<10^4$ mol^{-1} dm^3) [12, 19, 21] in almost same condition, indicating that $-OCH_3$ group or allyl in phenol can enhance the binding ability of guest with CDs. These results show that the matching between cyclodextrin cavity volume and guest dimension, and the substitute groups' essentiality in both end side of the cavity plays an important role in the formation and stability of inclusion compound of a substituted phenol with CDs or their derivatives.

Conclusions

The inclusion action of eugenol with α-, β-, γ- and DMβ-CD were investigated in solid state and in aqueous solution in this paper. The solid inclusion compounds of eugenol-β-CD and eugenol-γ-CD were prepared whereas those of eugenol with α- and DMβ-CD were not obtained under the same condition, indicating that water-solubility of the latter is much higher than the former. The inclusion phenomena of eugenol with β- and γ-CD were successfully characterized by XRD, FT-IR spectroscopy, TG, DSC in the solid state and verified by UV-visible spectroscopy and NMR spectroscopy in aqueous solution. The K values of eugenol with α-, β-, γ- and DMβ-CD are 4.95×10^4, 3.96×10^5, 1.47×10^5 and 9.33×10^4 mol^{-1} dm^3, respectively, which are in the same order of magnitude except for the first one, suggesting that the matching between cyclodextrin cavity volume and guest dimension has a great influence on the formation and stability of inclusion compound of a substituted phenol.

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